Communications to the Editor

The Mechanism of Hydrogen-Transfer Polymerization

There have been numerous reports concerning hydrogen-transfer polymerization since the initial description of the base-catalyzed polymerization of acrylamide to poly-β-alanine by Breslow, Hulse, and Matlack 10 years ago.[1] However, little has been done to elucidate the mechanism.

Two alternative schemes (eq 1 and 2) were suggested originally as initiation reactions.[1] Considerable evidence has accumulated that reaction 1, which was favored initially because of the unsaturation found in the polymer, is the actual initiation reaction when sodium or potassium *t*-butoxide is used as the catalyst. Thus, Stephens[2] isolated N-sodium and N-potassium acrylamide from the treatment of acrylamide with sodium and potassium *t*-butoxide, respectively; reaction with ethyl bromide gave a 45% yield of N-ethylacrylamide. Tani, Oguni, and Araki[3] isolated a mixture of N-benzylacrylamide and 3-*t*-butoxypropionamide from a reaction using sodium *t*-butoxide and benzyl chloride. More definitively, Trossarelli, Guaita, and Camino[4] polymerized acrylamide with alcohol-free sodium *t*-butoxide and recovered the theoretical amount of *t*-butyl alcohol from the reaction mixture.

$$CH_2{=}CHCONH_2 + B^- \rightleftharpoons \underset{\text{I}}{CH_2{=}CHCONH^-} + BH \qquad (1)$$

$$CH_2{=}CHCONH_2 + B^- \rightleftharpoons \underset{\text{II}}{B{-}CH_2CH\overset{-}{C}ONH_2} \rightleftharpoons B{-}CH_2CH_2CONH^- \qquad (2)$$

On the other hand, it seems that sodium methoxide adds to the double bond of acrylamide, as indicated by Ogata[5] and proved by Tani, Oguni, and Araki,[3] by the isolation of 3-methoxypropionamide from the reaction mixture. However, for reasons stated below we feel that the actual initiation reaction is 3 and not 2.

$$B{-}CH_2\overset{-}{C}HCONH_2 + CH_2{=}CHCONH_2 \rightleftharpoons B{-}CH_2CH_2CONH_2 + CH_2{=}CHCONH^- \qquad (3)$$

Two alternative schemes for propagation were also suggested in the original paper.[1] One involves an intramolecular hydrogen transfer in each step (reaction 4).

$$-CH_2CH_2CONH^- \xrightarrow{M} -CH_2CH_2CONHCH_2\overset{-}{C}HCONH_2 \longrightarrow -CH_2CH_2CONHCH_2CH_2CONH^- \xrightarrow{M} \text{etc.} \qquad (4)$$

The other involves an intermolecular hydrogen transfer in each step (reaction 5). Reaction 5 was preferred for two reasons: the unsaturation found in the polymer and the broad molecular weight distribution. Thus, products ranging from a compound analyzing reasonably well for unsaturated dimer (III) to high polymer were found in the reaction mixture. However, Ogata[5] reported that he could not find any unsaturation in his polymer and postulated initiation by addition to the double bond (reaction 2) and propagation involving intramolecular hydrogen transfer (reaction 4). This mechanism is frequently cited,[6,7] in spite of the fact that the formation of III and other terminally unsaturated products has been confirmed on several occasions.[8-10]

$$CH_2{=}CHCONH^- \xrightarrow{M} CH_2{=}CHCONHCH_2\overset{-}{C}HCONH_2 \xrightarrow{M} \underset{\text{III}}{CH_2{=}CHCONHCH_2CH_2CONH_2} + CH_2{=}CHCONH^- \longrightarrow \text{etc.} \qquad (5)$$

In order to differentiate between the two mechanisms the disappearance of acrylamide was determined as a function of time. Mechanism 4 should have the normal attributes of an addition polymerization reaction, *i.e.*, monomer should disappear according to some simple rate law while high polymer is being formed, since it is difficult to see why the necessary intramolecular hydrogen rearrangement should affect this fundamental mode of chain growth. Mechanism 5, however, should have all the attributes of a condensation polymerization, *i.e.*, at the start of the polymerization monomer is converted to dimer, trimer, etc.; gradually these pieces combine until eventually, long after monomer has disappeared, high polymer begins to form.

A 10% solution of acrylamide in dry sulfolane, containing 0.04% phenyl-β-naphthylamine to prevent radical polymerization, was heated to 100° and 1.8 mol % of potassium *t*-butoxide was injected as a 3.1% solution in *t*-butyl alcohol. After stirring for 2 min at 100° the polymerization was quenched with 1 *M* sulfuric acid and the acrylamide concentration determined by vpc analysis. By comparison of the peak areas of known acrylamide concentrations with the polymerized sample it was shown that 90% of the acrylamide had disappeared in 2 min; no high molecular weight polymer was present after 5 min. In a similar experiment using pyridine as the solvent, 70% of the monomer had disappeared within 2 min; no high molecular weight polymer was observed after a 10-min polymerization time. In control experiments both the sulfolane and pyridine reactions gave significant yields (>60%) of high molecular weight, water insoluble polymer with extended polymerization times (>2 hr). Therefore, acrylamide monomer disappears long before high molecular weight polymer is observed.

There would appear to be little doubt, therefore, that the propagation step in the hydrogen-transfer polymerization of acrylamide in the presence of *t*-butoxide involves an intermolecular hydrogen transfer, first to monomer, then to dimer, trimer, etc. (mechanism 5).

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(1) D. S. Breslow, G. E. Hulse, and A. S. Matlack, *J. Amer. Chem. Soc.*, **79**, 3760 (1957).

(2) J. R. Stephens, U. S. Patent 3,084,191 (1963).

(3) H. Tani, N. Oguni, and T. Araki, *Makromol. Chem.*, **76**, 82 (1964).

(4) L. Trossarelli, M. Guaita, and G. Camino, *ibid.*, **105**, 285 (1967).

(5) N. Ogata, *ibid.*, **40**, 55 (1960).

(6) R. W. Lenz, "Organic Chemistry of Synthetic High Polymers," Interscience Publishers, Inc., New York, N. Y., 1967, p 473.

(7) A. Ravve, "Organic Chemistry of Macromolecules," Marcel Dekker, Inc., New York, N. Y., 1967, p 272.

(8) H. Nakayama, T. Higashimura, and S. Okamura, *Kobunshi Kagaku*, in press; *Polym. Prev.*, **3**, 27 (1967).

(9) Ferrania S. p. A., Belgian Patent 685,690 (1967).

(10) Y. Iwakura, N. Nakabayashi, K. Sagara, and Y. Ichikura, *J. Polym. Sci., Part A-1*, **5**, 675 (1967).

Inasmuch as the presence of unsaturation in the polymer has been demonstrated on several occasions, initiation under these conditions is by acrylamide anion.

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Craze Formation Yield Stress and the So-Called Ductile–Brittle Transition in Glassy Polymers

The purpose of this communication is to add to the growing body of evidence favoring the view that the so-called ductile–brittle transition in glassy polymers is in reality a transition between two alternate modes of ductility both of which, prior to specimen fracture, can involve large amounts of straining in large amounts of polymer. We also wish to suggest that accumulated evidence makes difficult the view that gross polymer ductility is fully explained by the hypothesis that under stress T_g is caused to be equal to or lower than the actual temperature of the deforming polymer.

Below their T_g's linear amorphous polymers like polystyrene, polymethyl methacrylate, polycarbonate, and poly-2,6-dimethylphenylene oxide (PPO®)[2] resin commonly exhibit ductile failure by a shear deformation mechanism over temperature ranges which vary from 15 to 300°. Little or no density change is involved. The temperature range over which this behavior can be observed can be extended (a) by careful choice of testing rate;[1] (b) by preorientation of the specimen at $T > T_g$;[3a] or (c) by conducting the test under hydrostatic pressure.[3b]

Below the so-called ductile–brittle transition temperature the common mode of failure is apparently brittle in that no maximum is observed in the stress–strain curve. Crazing initiates at low stress, fracture initiates in one of the crazes,[4] and more craze material is produced as the crack propagates.[5] The high energy of crack propagation is associated with the viscoelastic strains involved in the craze formation and breakdown.[6]

Experimental Section. In the course of studies of the role of organic agents in promoting craze formation and breakdown in glassy polymers, we have noticed large differences in mechanical response of PPO films tested in the presence of small-molecule organic agents. These differences depend on whether the agent is applied at the initiation of the tensile test or is allowed to absorb in the specimen to equilibrium prior to test initiation.

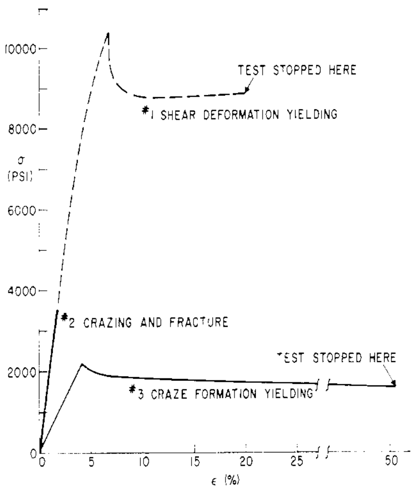

Figure 1. Engineering stress–strain curves for PPO film at 0.05 in./min extension rate: test 1, dry film; test 2, film immersed in acetone at start of test; test 3, film equilibrated with acetone vapor prior to test initiation.

In Figure 1, for example, we show three Instron stress–strain curves at 0.05 in./min elongation rate for 2.5-mil thick annealed film specimens of PPO of $[\eta] = 0.71$ dl/g. Specimens had the conventional dogbone shape with a gauge length of 1.25 in. Curve 1 is the engineering tensile stress–strain curve of the dry film; a yielding of the well known type involving response to the shear component of stress[7,8] occurs at 10,400 psi. Curve 3 exhibits apparently brittle fracture at 3500 psi, the crack having initiated at a single preformed craze; for this test the film specimen was mounted in a special jig which allowed simultaneous initiation of straining and immersion of the film in liquid acetone.

Curve 3 was obtained from testing a specimen which had been mounted in the same jig with a few cubic centimeters of acetone in the bottom of the glass envelope enclosure and left in contact with the saturated vapor for 24 hr prior to test initiation. (From separate sorption kinetic experiments this film is known to reach sorption equilibrium in acetone in 24 hr; equilibrium solubility is 0.16 g/g of polymer. The equilibrated film is still glassy at room temperature as evidenced by its lack of plasticizer-induced crystallinity[9] and its modulus of 4×10^9 dyn/cm^2.) Crazes were observed to initiate at low stresses and grow very rapidly, each tending to cover the entire cross section. Craze formation accelerated with stress increase, and it was apparent that the yield stress observed (2200 psi) was to be construed as that stress at which plastic deformation by craze formation equaled the rate of crosshead extension. The test was continued to about 50% elongation of the test section and then stopped because of limitations in the testing jig. At no time were there observed any signs of deformation bands at angles other than 90° to the tensile stress direction; thus shear deformation is ruled out as contributing significantly to the ductile failure observed here.

Figure 2 is a photomicrograph of the test section of specimen 3 subsequent to testing. The corrugations running perpendicular to the stress direction are the edge grooves of crazes. It is apparent that the fraction of the area taken up by crazes $F \simeq 0.5$. We may estimate crudely the fraction f of the original test section which has been converted into crazes as follows. From craze refractive index measure-

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(1) R. E. Robertson, private communication.

(2) Registered trademark of the General Electric Co.

(3)(a) R. D. Andrews and W. Whitney, Massachusetts Institute of Technology Textile Division Report No. TD-123-64, May 1, 1964. (b) L. Holliday, J. Mann, G. Pogany, H. Pugh, and D. Gunn, *Nature*, **202**, 381 (1964).

(4) J. P. Berry, *J. Polym. Sci.*, **50**, 107, 313 (1961).

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(6) R. P. Kambour, *ibid., Part A-2*, **4**, 17, 349 (1966).

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